

Bader's interatomic surface and Bohmian mechanics.

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Abstract

A Thomas-Fermi statistical analysis of Bader's interatomic surface developed in a previous work [1] is here extended by considering exchange effects and electron density's inhomogeneity at basic level via Thomas-Fermi-Dirac-Weizsacker model. The results obtained show interesting connections with bohmian mechanics and lead to a statistical interpretation of the chemical properties of condensed systems at atomistic level.

I. INTRODUCTION

In a previous work [1] we analyzed the statistical meaning of Bader's interatomic surface (or zero flux surface of the electronic density gradient), i.e.

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n} = 0, \forall \mathbf{r} \in S(\mathbf{r}) \quad (1.1)$$

(where \mathbf{n} is the unit vector perpendicular to $S(\mathbf{r})$ at each point \mathbf{r} of the surface S).

We used the approximation of Thomas-Fermi for the electron density and related properties and showed that the partitioning of the whole system in subsystems which are in mutual statistical equilibrium is consistent with Bader's partitioning of atoms in molecules. The Theory of *Atoms in Molecules* is well known, thus we do not review it and suggest the reader to consult the following references [2–7], while for technical applications see for

example [8–14]. The central point of our previous work was to define the electronic chemical potential within the approximation of the simple Thomas-Fermi model and then consider two cases, electron as non interacting particles, and electrons as classical interacting particles. Next, by imposing the condition of statistical equilibrium at each point of the surface of separation between two subsystems, which means the gradient of the electronic chemical potential at the surface to be zero along the crossing direction (normal to the surface), we could comment on the consistency between Bader’s definition and the statistical definition of atomic subsystem in a multiaatomic system. In this work we extend the previous analysis to a more sophisticated Thomas-Fermi model which takes into account exchange energy (Dirac) and the inhomogeneity of the electron density, i.e. the Weizsäcker correction to the Thomas-Fermi kinetic energy; the resulting model is known as Thomas-Fermi-Dirac-Weizsäcker (TFDW) (see pg 127-136 of [15]). We apply the procedure developed in our previous work and find some interesting connections with bohmian mechanics (for details about bohmian mechanics see for example [16–18] and references therein). This is an interesting result since an attempt to interpret Bader’s theory in terms of bohmian mechanics has already been done for the part relative to the chemical bond [19–21]; our current results can be integrated with those and lead to a simple interpretation of some chemical concepts in a statistical context with evident advantages for molecular modeling and its applications.

II. THOMAS-FERMI-DIRAC-WEIZSACKER MODEL

The introduction in the simple Thomas-Fermi energy functional

$$E_{TF} = C \int_V \rho(\mathbf{r})^{5/3} - \sum_{i=1,M} Z_i \int_V \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_i|} d\mathbf{r} + \frac{1}{2} \int \int_V \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (2.1)$$

(where C is a proper dimensional constant, V is the total volume of the system, the first term represents the kinetic energy within the Thomas-Fermi approximation, the second term describes the total interaction between electrons and nuclei (Z_i, \mathbf{R}_i represents the charge and position of the i -th nucleus, while $i = 1, M$)) of the exchange energy term $-C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}$

where C_x is the appropriate dimensional constant and the Weizsäcker correction term to the kinetic energy $\frac{\hbar^2}{8m} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}$, leads to the, so called, TFDW energy functional:

$$E_{TFDW} = C \int_V \rho(\mathbf{r})^{5/3} - \sum_{i=1,M} Z_i \int_V \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_i|} d\mathbf{r} + \frac{1}{2} \int \int_V \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' - C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r} + \frac{\hbar^2}{8m} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \quad (2.2)$$

Within this approximation the electronic chemical potential $\mu(\mathbf{r})$ is derived via a variational procedure as

$$\mu(\mathbf{r}) = \frac{\delta E_{tot}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (2.3)$$

and this leads to the following relation:

$$\mu(\mathbf{r}) = \frac{5}{3} C \rho(\mathbf{r})^{2/3} - \sum_{i=1,M} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \frac{1}{2} \int_V \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \frac{4}{3} C_x \rho(\mathbf{r})^{1/3} + \frac{\hbar^2}{8m} \left[\frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2} - 2 \frac{|\nabla^2 \rho(\mathbf{r})|}{\rho(\mathbf{r})} \right]. \quad (2.4)$$

Now we impose the statistical equilibrium $\mu(\mathbf{r}) = \text{constant}$ at the interatomic surface S' along the normal crossing direction, i.e.

$$\nabla_{\mathbf{n}} \mu(\mathbf{r}) = 0 \quad (2.5)$$

$$\forall \mathbf{r} \in S'(\mathbf{r}). \quad (2.6)$$

In order to understand a possible meaning of Bader's surface S in a statistical context, let us suppose that S and S' coincide, which means that we suppose Bader's topological partitioning criterion is equivalent to a statistical partitioning criterion of $\rho(\mathbf{r})$, this will allow us to apply the properties of S to Eq.2.5 (of course S in Eq.1.1 and S' in Eq.2.6 are not necessarily the same and will comment on this case later on); i.e. taking into account that $\nabla \rho(\mathbf{r}) \cdot \mathbf{n} = 0, \forall \mathbf{r} \in S(\mathbf{r})$ we obtain

$$\nabla_{\mathbf{n}} \left[- \sum_{i=1,M} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \frac{1}{2} \int_V \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\hbar^2}{8m} \left[\frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2} - 2 \frac{|\nabla^2 \rho(\mathbf{r})|}{\rho(\mathbf{r})} \right] \right] = 0. \quad (2.7)$$

Since $- \sum_{i=1,M} \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|} + \frac{1}{2} \int_V \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \phi(\mathbf{r})$ is the classical electrostatic potential, Eq.2.7 expresses the condition that the generalized force which takes into account non-local (and

non-classical) effects must vanish at the surface of separation. The interpretation of the above result is the same furnished in our previous work, with the exception that now we do not simply have the classical electrostatic force but an additive term, as one could have easily guessed *a priori*. However what makes this result interesting is the fact that the term $\frac{\hbar^2}{8m} \left[\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})^2} - 2\frac{|\nabla^2\rho(\mathbf{r})|}{\rho(\mathbf{r})} \right] = Q(\mathbf{r})$ represents the Bohm potential (see [19]). This consideration, will allow us to interpret the results found so far in terms of bohmian mechanics.

III. BADER'S THEORY AND BOHMIAN MECHANICS

We supposed that S and S' are the same, i.e. Bader's interatomic surface corresponds to a surface of separation between two statistical subsystems in equilibrium. S (or S') does not explicitly show the nature of the bond at the separation, but only define the topological domain of each atom. This means that this analysis furnishes one chemical information (defines atomic entities) but does not show how they are related to each other in chemical terms. In their work [19] Levit and Sarfatti shows that Bohm's quantum potential can give a direct interpretation, at least for atoms not beyond the third row as underlined by Hamilton [20,21], of bonding and reactivity in a multiatomic system. In the light of what stated above let us consider the concept expressed by Eq.2.7, i.e. the electrostatic potential $\phi(\mathbf{r})$ must be equal to minus Bohm potential $Q(\mathbf{r})$ at every point of the surface S . This means that from the topology of $-\phi(\mathbf{r})$ one can work out the bonding nature and reactivity at each point of the separation surface, i.e. along S bonding and reactivity can be determined in terms of classical electrostatic interaction.

One can notice that in general, in case S and S' are not the same (i.e. $\nabla\rho(\mathbf{r}) \neq 0$), it is possible to say that along S' bonding and reactivity are equivalently described by a quantum (Bohm potential) or a classical (E_{TF}) approach.

Although the model used is highly simplified, as extensively discussed in our previous work, the conclusions above are very interesting because furnish basic indications about the nature of chemical properties in a statistical context stimulating a further development at

higher level of theory.

As stated in our previous work, rigorously speaking, the force which acts at the surface of an atom is the Ehrenfest force and the results obtained here are valid only within the approximation done for exchange and density's inhomogeneity. At higher level of approximation for exchange and correlation, the physical picture may be very different; nevertheless starting from our results one could build a more complete and rigorous picture. We have found also another connection with bohmian mechanics in terms of single particle dynamics. In this case we have to consider the quantum wavefunction to be imaginary and in polar form $\psi(\mathbf{r}) = R(\mathbf{r}, t)e^{iS(\mathbf{r}, t)}/\hbar$, or the more familiar $\psi(\mathbf{r}) = (\rho(\mathbf{r}, t)^{-1/2})e^{iS(\mathbf{r}, t)}/\hbar$ where $\rho(\mathbf{r}, t)$ is the one particle time dependent electron density as considered so far. The point particles of mass m in the configuration space will be governed by the following dynamics:

$$v_n = \frac{\hbar}{m} I_m \frac{\nabla_n \psi}{\psi} \quad (3.1)$$

where v_n is the velocity of the particle along the direction \mathbf{n} . Applying the Shröedinger equation and considering the stationary case, using the property $\nabla \cdot v_n = \frac{\partial v_n}{\partial n}$ where $\frac{\partial}{\partial n}$ is the derivative with respect to the direction normal to the surface S , from equation (2) in Ref. [17] we obtain:

$$\frac{\partial v_n^2}{\partial n} = -\nabla_n \left(\frac{1}{m} \phi(\mathbf{r}) + Q(\mathbf{r}) \right) \quad (3.2)$$

($\nabla_n = \mathbf{n} \cdot \nabla$, and \mathbf{n} as specified before is the vector normal to S at each point). Considering S and S' coinciding, from Eq.2.7 and Eq.3.2 one obtains:

$$v_n \frac{\partial v_n}{\partial n} = 0 \quad (3.3)$$

Eq.3.3 is satisfied either in case the velocity of the particle normal to S is zero or in case the flux of kinetic energy is zero. In the first case we have a natural interpretation on interatomic surface, i.e. the particle does not cross the border and so belongs to a particular topological domain, in the second case, this expresses the fact that the flux of classical kinetic energy in the Thomas-Fermi formulation $\frac{\nabla \rho}{\rho^{1/3}}$ and the flux of the quantum kinetic energy $v_n \frac{\partial v_n}{\partial n}$

through the surface S are both zero. These properties of S are very interesting and, as the properties previously shown, stimulate further investigation of the classical-quantum connections of S . However one must notice that although this latter result is intriguing, it applies only to complex wavefunctions; this means that for practical application in current research, where ground state calculations are mainly done, this result cannot be used unless particular cases are investigated (e.g. systems in magnetic fields).

IV. DISCUSSION AND CONCLUSIONS

We analyzed the statistical meaning of interatomic surface in Bader's formulation from a statistical point of view within the approximation of Thomas-Fermi-Dirac-Wiezsacker. It emerged an interesting connection with bohmian mechanics in interpreting properties of points at the surface S in terms of bonding and reactivity. It must be also clear that this analysis is valid in the limit of the approximations done, more sophisticated models could lead to different results and certainly not to a direct interpretation in terms of bohmian mechanics. However it would be interesting to understand why and how the modification of properties of S occur at higher level of theory using our previous analysis as a starting point. Another important problem is to understand how S and S' are connected for real cases; our analysis was based on the hypothesis that they do coincide, so that we could comment on the consistency of Bader's surface with a statistical definition but this hypothesis is not obvious and if they differ it would be interesting to understand at which level of approximation they do coincide. Since Bader's procedure to obtain S is based on a rigorous method within quantum mechanics, the exact relation between S and S' at different levels of statistical theory could lead to clearer formulation of quantum properties in statistical terms with obvious advantages for practical applications. In conclusion, we think that our analysis is important for a formulation in statistical terms of the chemical properties at atomistic level and because represents a stimulating challenge for further developments.

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